Quantifying CO$_2$ leak rates in aquatic environments

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Abstract

The Daylesford region of Victoria (Australia), is a region of natural CO$_2$ seepage. Small bubble streams of CO$_2$ are released into ephemeral river beds proximal to mineral springs that contain high dissolved CO$_2$ content. We study four sites of CO$_2$ degassing to (i) establish the characteristics of CO$_2$ seepage caused by transport to surface of CO$_2$-rich water, (ii) provide an estimate of CO$_2$ flux in the region, and (iii) investigate seasonal effects on CO$_2$ seepage. We observe that bubbling behavior varies considerably between sites, including the number and distribution of bubbling points, and bubble stream the continuity. Total CO$_2$ seep rates at each site were low (< 20 kg/d) but varied substantially between different sites. There were no obvious indicators of total emission rate; the bubble density or other characteristics at the highest emission seep were not remarkably different to the smaller seeps. We find that the total CO$_2$ emission varies inconsistently with season, with some seep rates increasing and other decreasing in the dry season when water levels are lower. We find there are challenges in quantifying the total gas leakage at sites of highly localized and intermittent degassing. Our work has implications for detecting and quantifying leaks from engineered CO$_2$ storage sites which emerge in aqueous environments, which could be these are marine or terrestrial (lakes or rivers).

Keywords: Leakage; monitoring; natural analogue; seasonality

1. Introduction

It is important to demonstrate storage site monitoring capability to assure regulatory bodies and the public of CO$_2$ storage integrity [1]. This includes the capability to identify and quantify potential CO$_2$ leakage. A significant proportion of global CO$_2$ storage capacity is located offshore, with some regions of the world having no onshore storage [2]. In the case of CO$_2$ migration from offshore stores, should the leaked CO$_2$ migrate to the seabed it will emerge as bubble plumes that dissolve into the water column [3, 4]. Recent work has identified that the current ability to quantify CO$_2$ leakage into the marine environment is limited due to a number of reasons, including sampling challenges [5]. In the case of CO$_2$ migration from engineered stores onshore, if the leaked CO$_2$ migrates to the near surface it could dissolve into groundwater and perhaps emerge as a dissolved constituent of natural springs, seep to the atmosphere as a dry gas, or seep into water bodies such as lakes or rivers. Indeed, studies of onshore natural analogues and field sites find that CO$_2$ seepage tends to occur in topographic low points [6, 7] where there may be rivers or lakes. The majority of onshore CO$_2$ release experiments conducted around the world to date have found it problematic to estimate the proportion of injected CO$_2$ that leaked to surface [7]. Similarly, the observations and challenges at the world's only offshore CO$_2$ release experiment, QICS, illustrated the need to develop and test

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techniques to measure and quantify the fate of injected CO_2 in the marine environment [8]. It is therefore important to establish methods that would be most appropriate for calculating leakage into aqueous environments whether terrestrial or marine.

Here, we studied natural CO_2 seeps in the Daylesford region in the Central Highlands of Victoria (Australia), to investigate how well CO_2 seepage can be quantified at these sites. In the Daylesford region over sixty mineral springs rich in dissolved CO_2 have been documented [9]. These seeps largely occur as bubble streams in creeks or water bodies close to mineral springs with high CO_2-content. We surveyed degassing characteristics and flux during two field seasons; in June 2016 and March 2017 (wet season and dry season respectively, to compare seasonal effects on CO_2 leak rates) at three locations where CO_2 bubbles through ponded spring-water discharge; Wombat Flat, Taradale, and Tipperary Mineral Springs. This is the first time that CO_2 emission rates from these natural seeps have been quantified.

1.1. Hydrogeology of the Daylesford region

Three principal units define the geology of the Daylesford region: deformed Ordovician turbidites of the Lachlan Fold Belt intruded by Devonian granites and overlain by Quaternary basalts. These basalts represent intraplate volcanism occurring between 4.6 Ma until as recent as 5 ka ([9] and references therein). The turbidites represent a 4500 m-thick sequence of greenschist facies slates, shales, and sandstones that were extensively folded, fractured, and faulted during mountain building in the Devonian. The regional structure is dominated by NNW trending folds and faults associated with this deformation event, and gold-bearing reefs in the fold hinges and faults were the target for miners. The turbidites and the overlying basalts form regional fractured aquifers [10]. Faults, joints, fractures and cleavage in the Ordovician bedrock facilitate groundwater and mineral water circulation, and the region has two distinct groundwater systems; a shallow fresh groundwater system and a second deeper mineral water system [10]. These mineral waters have a residence time of ~4.5 ka [11], have unique chemistries, and are effervescent, but there is no appreciable thermal anomaly between the mineral waters and the surrounding groundwater. The dissolved gas in the mineral waters is predominantly CO_2 and their it's gas signature indicates a mantle source [12], assumed related to the Quaternary volcanism. While the Daylesford mineral springs and the total dissolved CO_2 content of the mineral waters is consistent across the region [13], the geochemistry of individual springs is variable and is controlled by highly localised fluid-rock interactions facilitated by elevated CO_2 partial pressures [14].

The mineral springs are of historic and economic importance to the region, attracting commercial water bottling operations, health spas, and tourism since Victorian times. The spring locations and their chemistry are therefore well studied, and the mineral waters are protected by the Department of Environment, Land, Water and Planning, Victoria. The mineral springs typically occur in streambeds where the water table intersects the ground surface, but at many locations around Daylesford the springs have been developed to improve access, for example by installing hand pumps to draw mineral waters from a borehole. These wellbores tend to target faults or anticline structures, as gassy flow tends to occur in these highly fracture horizons. Reports of CO_2 gas emissions are documented, often close to natural mineral spring eye, as are tufa-type deposits which indicate previous sites of seepage and gas emission [15].

2. Methods

2.1. Field Campaigns

The climate in the Daylesford region is marked by wet winters and hot, dry summers. Two field campaigns were conducted to investigate CO_2 emissions from mineral springs in the Daylesford region and to investigate seasonal influences on CO_2 natural seepage.

The first field campaign was undertaken during June 2016 (i.e. winter, during the wet season). The fieldwork aimed to scope seepage sites suitable for investigation and to collect initial estimates of CO_2 emissions. Six CO_2 sites were surveyed: Deep Creek, Glen Luce, Kyneton, Taradale, Tipperary and Wombat Flat (see Table 1 and Fig. 1). Deep Creek, Taradale, Tipperary and Wombat Flat were surveyed multiple times to investigate short-term variability in emission rate (i.e. over several days). Detail of the bubble stream locations were not collected during the 2016 campaign.

The second field campaign was in March 2017 (i.e. early autumn, the end of the dry season). The fieldwork aimed to complete CO_2 flux surveys and also conduct detailed mapping of bubble stream locations. Due to time limitations, only three sites (Taradale, Tipperary and Wombat Flat) were studied in detail; Deep Creek was visited but not studied.

Table 1. Summary CO_2 seepage sites surveyed in the Daylesford region (Victoria, Australia)

| Site	Description	Location (Lat °)	Location (Long °)	2016 (wet season)	2017 (dry season)
				Survey dates	
Deep Creek	One of several mineral springs with gas emission associated locate along Deep Creek. Gas bubbling occurs in the creek bed, particularly at the edge of a concrete apron which caps the Deep Creek Mineral Spring (to channel the spring into the adjacent Victorian pump house)	-37.34911	144.074205	21/06/2016 23/06/2016 26/06/2016	23/03/2017
Glen Luce	Located in the river bed at a bend of the Loddon River. Gas bubbling occurs just upstream of two bores that tap the Glen Luce Mineral Spring.	-37.162250	144.222456	22/06/2016	n/a
Kyneton	Gas bubbling occurs towards the west bank of the Campaspe River, near its confluence with Boggy Creek.	-37.235916	144.420068	22/06/2016	n/a
Taradale	CO_2 degassing occurs in the center of the Back Creek around an old borehole (plugged in the 1990's) which is surrounded by a worn concrete platform.	-37.139467	144.349286	21/06/2016 22/06/2016 26/06/2016	22/03/2017
Tipperary	Located on the west bank of Sailors Creek, close to Tipperary Mineral Spring. Gas emission occurs in the creek bed to the east of and underneath a footbridge over the creek.	-37.337525	144.120144	22/06/2016 26/06/2016	23/03/2017
Wombat Flat	Located along the eastern margin of Lake Daylesford close to Wombat Flat Mineral Spring. Bubbling occurs in the lake shallows.	-37.349811	144.139869	24/06/2016 27/06/2016	22/03/2017
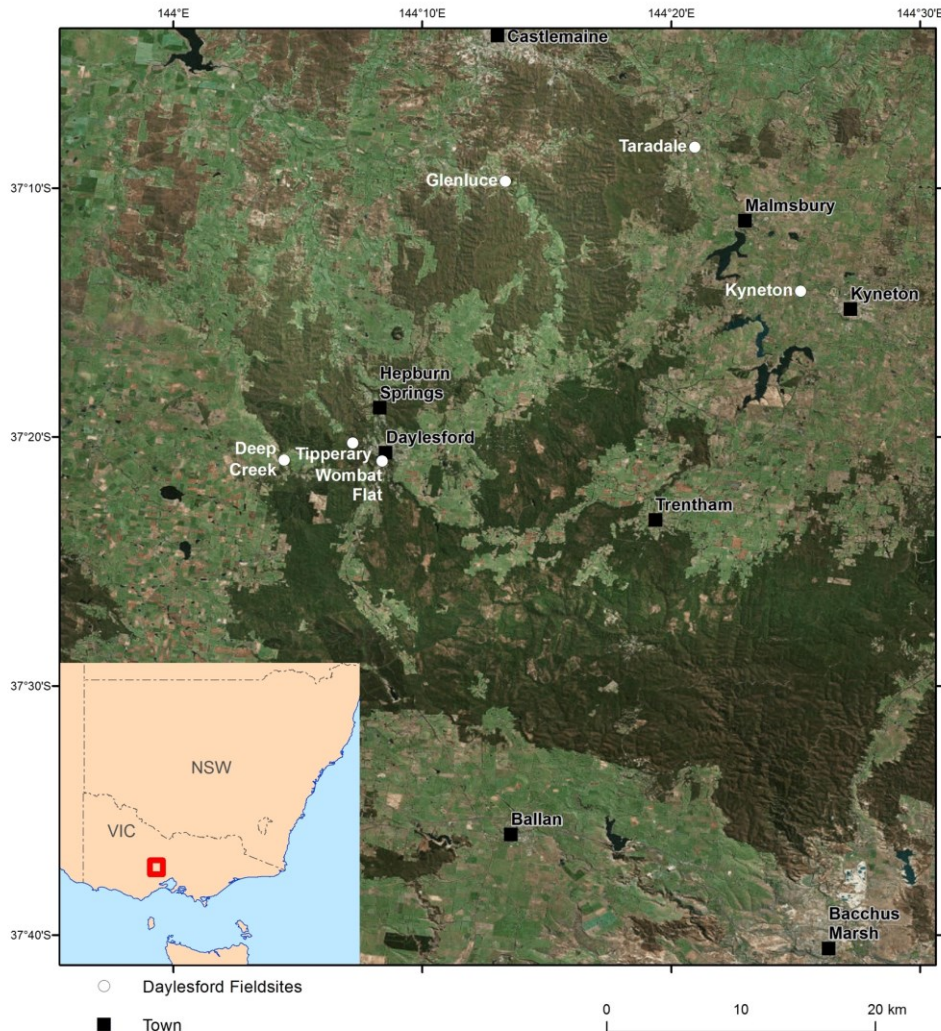
Fig. 1. Location map of sampled CO_2 seeps in the Daylesford region, Victoria, Australia

2.2. CO_2 measurements

CO_2 flux measurements were obtained using a West Systems portable flux system with attached accumulation chamber (type B) and LI-840A CO_2/H_2O gas analyzer following the method established by [16]. A hollow 50 mm PVC pipe frame was attached to the base of the accumulation chamber as a floatation device in order to facilitate flux sampling at the water surface. The base of the accumulation chamber was therefore slightly submerged in water and this change in volume was accounted for when applying the accumulation chamber constant, A.c.K, (a conversion factor between ppm/sec (instrument unit) and $g/m^2/d$). A.c.K temperature and pressure corrections were made using meteorological measurements recorded at Ballarat Airport (~40 km SW of Daylesford) where readings are taken at 10 min intervals. Where required, the floating flux chamber was attached to a pole to enable sampling of bubble streams without disturbing the creek sediments.

Flux measurements were taken at bubbling points (when bubbling was occurring, i.e. while the bubbling was active) and non-bubbling points across the pool to account for background diffuse degassing. The measurement period varied, but generally lasted for 90 s or longer, or until the accumulation in the chamber reached a CO_2 concentration of 20,000 ppm (at which point the accuracy of the gas analyzer is negatively impacted). Time restraints prevented the quantitative measurement of every identified bubble point, particularly where bubbling was extremely short-lived or

intermittent, and so our sampling focused on the most vigorous and continuous bubbling points in the interests of producing the most reliable upper bound estimate of the total CO_2 emission rate. The maximum bubble rate was determined using the West Systems Software (Flux Revision 3.99.4) and optimizing the flux integration for the maximum slope over 20 s. The measured flux was then multiplied by the area of the flux chamber to derive the CO_2 emission rate. This setting was found to capture the rate of the majority of the bubble streams, even if they were for a short duration. Background flux rates were integrated for the maximum linear regression coefficient (Errq) over 60 s.

2.3. Mapping CO_2 bubble locations

For the second field survey (March 2017), high precision GPS measurements of bubble stream locations and outcrop/creek features were taken using an Altus APS3G high precision GNSS survey system for Real Time Kinematic (RTK) position measurements. A base station was set up at each locality and the Rover recorded the UTM coordinates of the feature. The positional accuracy of the RTK equipment is < 1 mm, but human error positioning the RTK will be on the order of < 1 cm. There were some time delays and complications obtaining position measurements due to tree cover and, at Tipperary Mineral Spring, a footbridge which, in addition to the typically sporadic nature of the bubble streams, meant that the locations of the bubble streams were estimated using a local reference grid rather than the RTK. The bubble location error is therefore approximately ~10 cm.

3. Results

3.1. Site observations

Photographs of the seep sites visited in both field campaigns (Deep Creek, Taradale, Tipperary, and Wombat Flat) are shown in Fig. 2. The considerably wetter conditions during the June 2016 campaign resulted in more turbid conditions at the seepage sites (Fig. 2) and faster flowing streams (expect for at Wombat Flat, which is located next to Daylesford Lake). In contrast, the dry conditions of the March 2017 campaign meant lower water levels at the sites (especially Taradale and Tipperary). Indeed, for Deep Creek, Taradale, Tipperary (which are each located in different creeks, Table 1), the creek flow was very low or to stagnant whereas in June 2016 they had been full and flowing. The lower water levels in the dry season resulted in clearer water conditions but also greater quantities of surface algae at Taradale (Fig. 2d) and bacterial mats with visible iron staining at Deep Creek (Fig. 2b), Taradale (Fig. 2d) and Tipperary (Fig. 2f). Other authors note algal flocculates at the Daylesford mineral springs [15]. Analysis of algae from Taradale confirmed the presence of the cyanobacteria *Microcystis*, *Phormidium* and *Geitlernema*. The bacterial mats and iron staining are likely to be due to elevated concentration of dissolved Fe(II) in the spring water (up to 13 mg/L, [17]) and its oxidation to Fe(III). At Tipperary, the low creek level exposed adjacent outcrops of Ordovician sandstone and shale (Fig. 2f) and dry CO_2 seepage was detected from fractures within the outcropping sandstone [18].

June 2016 (wet season)	March 2017 (dry season)

Deep Creek

(a) View to South East. Episodic bubbling concentrated at prominent cracks in cement in the river bed, but also occurred elsewhere in the creek bed. Bubble locations were consistent for the three days surveyed. Area of observed degassing ~9 m x 4 m.

(b) View to North. The water in Deep Creek was flowing but shallow, and brown in colour. Bubbling was intermittent, and most concentrated near the bridge stand though could be observed <10 m either side. Area of observed degassing ~9 m x 4 m.

Taradale

(c) View to North East. Back Creek was flowing and quite deep in some parts of the Taradale pool. Bubbling was relatively consistent, and occurred in the creek bed and around the cemented bore. Area of observed degassing ~2 m x 3 m.

(d) View to North East. The water in Back Creek was not flowing, and the pool was choked with algae. Degassing occurred in several clusters close to the cemented bore, was episodic but at consistent location. Area of observed degassing ~1 m x 2.3 m.

Fig. 2. Photos and short description of CO_2 seeps visited in the wet (June 2016) and dry season (March 2017). Note the seasonal differences in the water levels and turbidity.

A film of bubbles was observed trapped under the algae at the surface of Taradale pool in the dry season (March 2017) (Fig. 3). These tended to be away from where bubbling was occurring since the bubble streams disturbed the water, keeping the surface relatively clear. The composition of these surface bubbles is presently unknown and is the subject of further studies. The trapped gas may have been CO_2 degassed from the pool (particularly as there were very high background CO_2 fluxes at Taradale). Alternatively, the gas may simply be O_2 produced by the cyanobacteria detected at the site.

Fig. 3. Algae and trapped bubbles observed at the surface of Taradale pool and location of CO_2 seepage

3.2. Bubble stream characteristics

We observe that CO_2 seeps in the Daylesford region occurs as bubble streams in creek beds close to mineral spring emissions. Bubbling may occur at the creek bank (Tipperary, Wombat Flat, Glen Luce, Kyneton), in the middle of the creek (Deep Creek, Taradale), or near to man-made or natural features, such as at the edge of – or fractures in - cement structures (Taradale, Deep Creek) or geological features such as bedding and fractures (Tipperary).

At all sites, bubbling was intermittent, that is, the observed bubble streams were not continuous, but we also observe that bubbling behavior varies considerably between sites. The distribution of bubbling points could be contained (< 1 m^2 at Wombat Flat) or more widespread (> 60 m^2 at Tipperary) and few (<20 points at Wombat Flat and Taradale) or numerous (>60 points at Tipperary). Some bubble streams were continuous, others were intermittent – usually short bubbling periods were followed by irregular periods of dormancy (from many minutes to half an hour, depending on the site). One bubbling points at Wombat Flat exhibited regular, cyclical activity, and others at Taradale demonstrated intermittent cyclicity. At some seeps, bubbling frequently and consistently occurred at select locations, whereas for others the bubble locations were much more variable with seemingly random changes in the location of active degassing. The size of the bubbles themselves also ranged from millimeter to centimeter scale, often dependent on the water depth, where larger bubbles emerge from deeper water. The characteristics of the bubble streams and their variability is summarized in Table 2.

Table 2. Bubble streams varied in their intermittency, rate, bubble size, and whether or not they emerged from specific features. The classifications described in the table capture the differences in the style of bubbling observed at the studied seeps.

Bubbling Style	Type	Description
1. Intermittency	A	Bubbling is mostly constant
	B	Bubbling is intermittent but cyclical (i.e. regular)
	C	Bubbling is intermittent and is not cyclical, but periods between bubbling are short i.e. bubbling is active more often than it is inactive (i.e. bubbling is 'on' more than it is 'off')
	D	Bubbling is intermittent and is not cyclical, but periods between bubbling are long i.e. bubbling is inactive more often than it is active (i.e. bubbling is 'off' more than it is 'on')
2. Rate	A	Bubbles in a single stream occur one after the other as a string of bubbles in quick succession
	B	The rate at which bubbles emerge varies.
	C	Bubbles in a single stream occur less rapidly; the bubbles do not form a 'string'
3. Size	A	Larger bubble size (causes lower pitched noise when the bubble(s) break the water surface)
	B	Bubble size variable
	C	Smaller bubble size (causes high pitched noise when the bubble(s) break the water surface)
4. Source	A	Bubble emerges from geological structure such as bedding/foliation plane, or fracture. Or from man-made feature, such as a crack in cement.
	B	Bubble emerges from sediment or gravel in the river bed
	C	Bubble obscured/not visible.

3.3. CO_2 emission rates

The background CO_2 flux and CO_2 bubbling rates for the four field sites visited in both field seasons are shown in Table 3. CO_2 seep rates varied substantially between different sites; the highest site average bubble emission was observed at Taradale during the June 2016 survey (330 g/d) and the lowest at Wombat Flat (8.2 g/d). In the first field campaign (June 2016, wet season), fluxes were measured on different days. We observed some variation in the location of the bubble streams and the total leak rate. However, the differences in the total leak rates measured days apart was comparatively low compared to differences between sites and between seasons.

All bubble streams at Taradale were intermittent but approximately the same number of bubble streams were observed during both seasons and in similar locations. For the other sites, Wombat Flat and Tipperary, much fewer bubble streams were observed during the wet season, particularly at Tipperary (61 vs 8 bubble streams). The higher water level and the flowing stream at Tipperary during the wet season is likely to mask many of the weaker or more infrequent bubble streams, making them more challenging to detect and to sample. Despite these differences, the magnitude of the average maximum bubble emission was found to be similar between both seasons for all sites.

The measured individual bubble stream rates from all four sites and across seasons ranged in value from 1.5 to 610 g/d (at Deep Creek and Taradale respectively, both in the wet season). Wombat Flat had the lowest rate of emission from individual bubble streams, whereas they were highest at Taradale in the wet season. The CO_2 emission rate will be a product of the period of bubbling activity, the rate of bubbling, and the bubble size, where bubble types (A) will be higher emitters than bubble types (C) for characteristics 1-3 in Table 2.

Background gas flux varied between sites, and also across each site, as shown in Table 3. The background fluxes also varied between the wet and the dry season seasons, particularly for Tipperary and Taradale (194 c.f. 29 g/m^2/d;

696 c.f. 24 g/m^2/d respectively, see Table 3). In both cases, in the wet season the creek was flowing whereas in the dry season the pools were isolated and seemingly stagnant. By comparison the mean background flux at Wombat Flat, which is located in a larger pool connected to Daylesford Lake was just 14 g/m^2/d in the dry season, only a little higher than the background flux measured in the wet season (8.2 g/m^2/d)

Table 3. Background flux and CO_2 bubbling rates for the four field sites visited in both field seasons, showing the range and the mean in parentheses. The measured background flux refers to gas flux measured from the water surface where there were no gas bubbles observed. The bubble rate refers to the maximum individual CO_2 emission rate for each of the bubble streams, where n = maximum total number of bubble streams observed at the site.

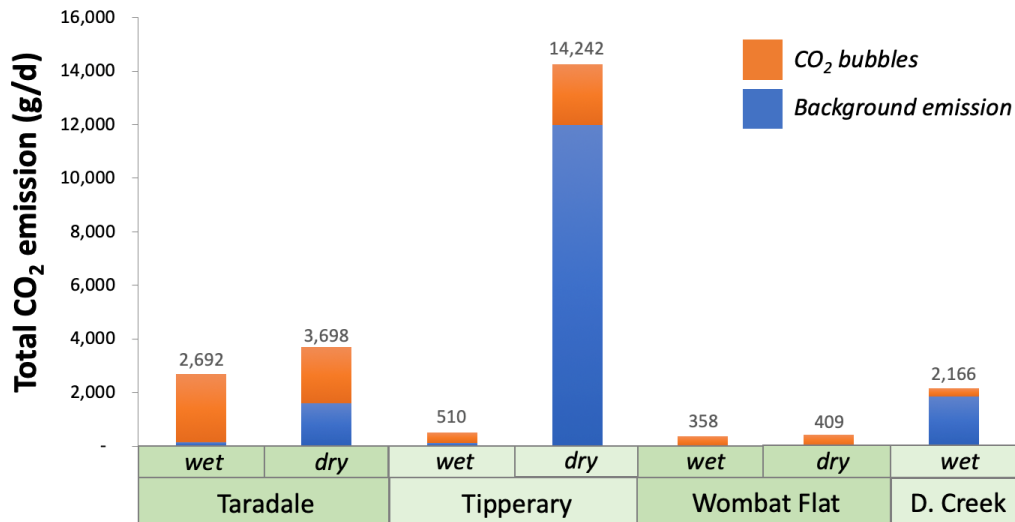|	June 2016 (wet season)			March 2017 (dry season)		
CO_2 seep	Background flux g/m^2/d (mean)	(n)	Max. bubble rate g/day (mean)	Background flux g/m^2/d (mean)	(n)	Max. bubble rate g/day (mean)
Wombat Flat	2.3-22 (8.2)	6	15-130 (69)	7.4 – 27 (14)	13	2.2-103 (30)
Tipperary	1.7 – 214 (29)	8	6.7 – 110 (60)	81-322 (194)	61	11-371 (90)
Deep Creek	7.1 – 154 (51)	13	1.5 – 470 (148)	n/a	n/a	n/a
Taradale	4.0 – 103 (24)	14	98 – 610 (330)	289-1965 (696)	17	15-525 (190)

Fig. 4. The total CO_2 emission for each CO_2 seep for the two seasons measured. The results also show the relative contribution to the total CO_2 emission from background CO_2 flux (CO_2 emission from water without visible bubbling) and the emission rate from the sum of the bubble streams (i.e. CO_2 emissions as bubbles). These values assume that gas bubbling at all locations is constant, and so will significantly overestimate the quantities of CO_2 being emitted. Background emission is calculated over the area defined by the lateral extent of the bubble distribution observed at each site and for each season (see Table 1), i.e. not the total area of the pool, river or lake.

4. Discussion

4.1. What controls the observed variations in CO_2 emission?

We find that background flux, total CO_2 emission and the style of bubbling varies between sites and between season. At all locations, fewer bubble streams were observed during the wet season, when the creek levels were higher and the streams were flowing. Deep and flowing streams will have greater potential for the uptake of the bubbling CO_2 compared to saturation/supersaturation in the low-flow or stagnant pools of spring water in the dry season. However the effect of season on the total CO_2 emission rate was inconsistent: total CO_2 emission was higher in the wet season for Wombat Flat and Taradale, and higher in the dry season for Tipperary. At all three studied seeps, the background emission was higher in the dry season than the wet season. In the dry season, not only were creek levels lower, but also algae were much more plentiful, both of which may affect the background.

Importantly also, the emission rate is not obviously indicated by bubble stream density nor total number of bubble streams (see Fig. 5); there was nothing remarkable about Taradale that suggested that it was the highest emitting seep, or that its emissions might be higher in the wet season. While we identify characteristics or variables that will affect the leak rate of the individual bubble stream such as bubble size, intermittency and rate of bubble release (see Table 2), the characteristics did not consistently vary between locations and seasons, and indeed larger bubbles did not necessarily mean larger gas emission; at Tipperary rapid emissions of small bubbles (Type 2A, 3C) could emit more gas than larger but shorter-lived bubble points (Type 1D, 2C, 3A).

The location of bubbles seemed fragile, as the bubble activity responded to sediment disturbance (e.g. treading close to the seep) and the number of bubble streams varied within seasons. However, the repeat surveys in the 2016 season tended to observe bubbles in similar locations, and the bubble locations between seasons were also notably similar, particularly at Taradale. This implies that while sediment and pressure disturbance may interrupt CO_2 flow, the seep pathways themselves are quite well established and constant. This is certainly the case at Taradale, Deep Creek and Tipperary where bubbling occurred at man-made or natural features.

The changing locations of the bubble streams indicates a very well-connected seepage system. The seepage of CO_2 from depth is probably (more) continuous, and may occur via more established flow pathways (e.g. fault zone or fracture). However in the near surface the flow will become intermittent due to water saturation of the flow pathways; CO_2 gas pressure must build enough to overcome the pressure of the water in the pore or fracture. Further, towards the surface, gases will be migrating through fractured rock units that are unloaded (and therefore more likely to be permissive) and river sediments. Should these flow pathways be highly connected, bubbling will become intermittent as flow paths turn 'on' and 'off'. Such temporal and spatial variability has been observed at other CO_2 seeps including Laacher See (Germany - CO_2 bubbling is observed from the floor of a crater lake), Panarea (Italy - submarine geothermal region) and at the QICS project (Scotland - simulated CO_2 leak to the marine environment) [8, 19].
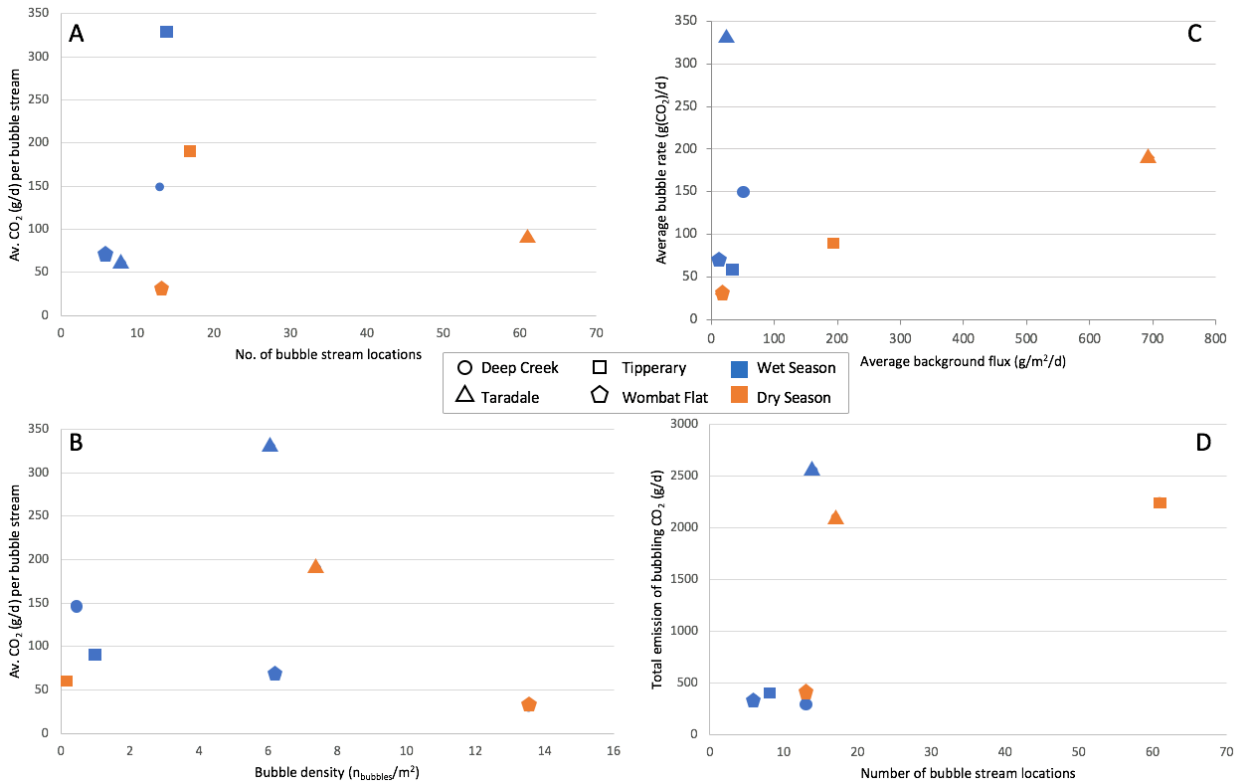
Fig. 5. The average CO_2 emission for each bubble stream is plotted against (A) the number of bubble streams counted and (B) the bubble density (i.e. the number of bubbles within the seep area) and (C) the average background flux. For (D) the total emission of CO_2 is plotted against the number of bubble stream locations at the site. None of these are very good indicator of the size of the CO_2 emission. This is likely to be because the bubble streams varied in their intermittency (including the period of activity and inactivity), their size, and how rapidly the bubbles were emitted during a period of activity.

Gassy mineral fluids in the Daylesford region are associated regional structures, often faults cutting anticline structures [15]. Down-hole camera surveys observe gas bubbles forming from the mineral waters around 20–30 m below the water table [10]. Such gas ebullition probably occurs as the waters depressurize during ascent or mix with unsaturated fluids, and the subsequent gas lift will enhance the mineral water flow. In the saturated zone free-phase CO_2 will be more buoyant than the surrounding groundwaters. It will therefore buoyantly migrate to surface, via available flow paths, perhaps dissolving into unsaturated groundwaters as it migrates, particularly if the saturated zone through which the gases flows is thick (i.e. the higher the groundwater table), unsaturated with CO_2, and the flow path is distributed rather than focused, and so offers more opportunities to interact with surrounding groundwaters. In contrast, when it reaches the vadose zone the CO_2 will no longer be more buoyant than its surroundings, for it is denser than air at ambient temperature. When groundwaters are low, CO_2 may spread out in the vadose zone, with less gas reaching the surface. Gas emission in the Daylesford region tends to be usually observed when the river levels are low [15]. Seasonal effects on CO_2 leak characteristics have been observed at other natural CO_2 seeps [20], and indeed seasonal impacts were explicitly explored at the Ginninderra CO_2 release experiment. Here, it was found that in the wet season, CO_2 leakage to surface was more concentrated and soil gas saturation reached 80%. In contrast, leakage was more distributed in the dry season, occurring in three smaller patches also associated with lower soil gas saturation (max. 60%). In addition, soil surveys aided by krypton tracer found that CO_2 spread much further from the horizontal well in the wet season [21], and it was hypothesized that the greater extent of the vadose zone in the dry season allows greater quantities of CO_2 to accumulate in the subsurface, and so limits the intensity of CO_2 release to surface [21, 22]. These effects may be observed at Tipperary and Taradale, where the measured CO_2 emission was substantially greater in the wet season.

4.2. Implications for CO_2 leak quantitation

The observed variations in seepage introduce complexities when attempting to measure gas fluxes and to estimate leakage rates at these sites. The standard approach to calculate total emission from flux rate necessitates ~constant rate of emission over a given area. So, what happens when, on the short term, the emission itself is inconsistently sporadic (bubbling intermittency), and the emission location changes unpredictably?

The approach used to integrate individual bubbles stream flux to calculate total emission rate presents a key quantification challenge; if bubbling intermittency (in time and location) is not accounted for, the flux will be overestimated. Further, physically measuring intermittent, short lived, and mobile bubble streams is challenging even when water depth is shallow and conditions benign. For high stream flow, it is likely for a survey to miss bubble streams that have short periods of activity and long periods of inactivity (Type 1D in Table 2), and therefore the estimated leak could be underpredicted. This might be the case at Tipperary in the wet season, where nearly 8 times more bubbling locations were observed in the dry season, but the bubbling points at Tipperary were particularly intermittent. Selecting the appropriate area for the background flux component of the total CO_2 emission introduces considerable uncertainty in the emissions estimate, especially if the background flux is elevated due to stagnant conditions (e.g. Taradale). Given the uncertainty with selecting a representative background area and the large variability between seasons (e.g. Tipperary, Table 3 and Fig. 4), it is debatable whether it is useful to include the background in the total emissions estimate. We observed much greater consistency between the average bubble rates between seasons compared to the background fluxes (Table 3).

Quantifying leakage to surface does not account for CO_2 dissolution into the pool. Where the pool was isolated, like Tipperary and Taradale in the dry season, the background fluxes were very high, suggesting the pool is saturated, and therefore gas will not be dissolving as it bubbles through the water. In contrast, in the wet season when there is water flow in the creek, the waters will not be CO_2 saturated and there is more capacity for CO_2 dissolution as it bubbles through the water. For this reason, for CO_2 quantitation at other aqueous seeps researchers have placed funnels over the bubble emergence (including QICS [4], Laacher See and Panarea [3]). Recent research indicates that the proportion of CO_2 that dissolves in the water is inversely proportional to the rate of CO_2 release [23], therefore, where pool/river waters are not saturated, the degree of solubilization may vary between bubble streams depending on the bubbling properties.

Importantly, regardless of the approach used to estimate total CO_2 flux, we find that flux nor total seep emission is not obviously indicated by bubble stream density nor total number of bubble streams (see Fig. 5); there was nothing remarkable about Taradale that suggested that it was the highest emitting seep, or that its emissions might be different depending on the season. Therefore, visible indicators are not useful for distinguishing whether rate of gas bubbling is orders of magnitude different (e.g. between Wombat Flat, ~30 g/d; Taradale, ~300 g/d).

However, despite these difficulties, even if the maximum emission rate is assumed to be constant for each bubble stream, then at all sites the total CO_2 emissions remain below <20 kg/d (including background flux).. For comparison, a single bubble stream at the QICS experiment emitted approximately 1 kg/d [4], and bubble locations at Panarea natural CO_2 site are as much as 370 kg/d [24]. It is questionable whether the scale of seepage at the mineral springs studied here would be detected if the bubbles were not being released into the creek bed where the bubbles are visible and therefore indicating leakage and focusing the scope of the field survey. Certainly there were no clues (e.g. visible or audible effect) to indicate the dry seepage detected at Tipperary [18]. Further work at the Daylesford seeps and other international sites should focus on low-intensity methods to estimate CO_2 leakage, for example, to explore whether there is an upper and lower bound for average bubble flow rate for low rates of seepage into aqueous environments which can be multiplied by the number of bubble streams and their characteristic intermittency (i.e. constant, active more often than inactive or vice versa) to get an order of magnitude estimate of the leak.

4.3. Relevance to CCS sites

Our observations, and the subsequent leak quantification challenges have implications of dynamic seepage on leak monitoring and quantification at engineered CO_2 storage sites. In the context of CCS, the Daylesford seeps are most representative of the leakage that could occur from the migration of CO_2 saturated brines towards the surface. At all sites the total CO_2 emissions remain below <0.01 t/d, or <4 t/yr. These emission rates are very small, and indeed are

negligible in the context of large-scale CCS. Further, in the dry season, seepage is occurring in low flow environments where waters are supersaturated and where background CO_2 emissions are very high and unrealistic for a range of other settings.

Regardless, even small emissions need to be able to be estimated, even if simply to show how small they are, particularly if seepage into rivers and lakes is most likely, owing to hydrology and the fact that buoyant fluids will seek paths with least or lowest overburden pressure. We suggest that magnitude emission rate classification of a leakage feature could be sufficient (e.g. <0.01 t/d, <0.1 t/d and <1 t/d) when using flux chamber techniques at small leak sites. At higher flux seeps (> 1 t/d) it may be possible to estimate leakage rates more accurately using atmospheric monitoring techniques, which are able to average out variability and better integrate emissions [25].

Further, it may not be enough to measure the CO_2 emissions to atmosphere from aqueous CO_2 seeps. CO_2 will be dissolving into the stream or lake water, and may well represent a very small proportion of the CO_2 which has leaked from depth, owing to CO_2 dissolution into groundwater and CO_2 dispersion in the vadose zone. CO_2 release experiment conducted to date have found that, depending on the environment and the release rate, a small proportion of leaked CO_2 may reach surface [7]. This therefore raises questions about when seepage is leakage; if leakage refers to CO_2 that migrates from the storage reservoir or complex, we need to be able to quantify the proportion of CO_2 lost during ascent to surface.

5. Conclusions

Our study of the style and quantity of seepage at four mineral springs in Daylesford, Victoria, and seasonal changes in emission rates have identified several challenges for quantitating CO_2 leakage. The first challenge is that of sampling intermittent and variable bubbling points where leakage rate is low. The second challenge is extrapolating the measured emissions into total emission from the site when bubbling is not constant. A third challenge is how to account for background flux where CO_2 saturation of the pond or river waters are high, and therefore are in effect represent a diffuse CO_2 seep. The fourth challenge is to consider what proportion of CO_2 that has leaked from depth has indeed made it to the earth surface. This work contributes to ongoing efforts to improve environmental monitoring techniques and quantitation approaches in the case of CO_2 leakage from engineered geological storage.

Acknowledgements

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